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Biolabile ferrous iron bearing nanoparticles in glacial sediments

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ABSTRACT

Glaciers and ice sheets are a significant source of nanoparticulate Fe, which is potentially important in sustaining the high productivity observed in the near-coastal regions proximal to terrestrial ice cover. However, the bioavailability of particulate iron is poorly understood, despite its importance in the ocean Fe inventory. We combined high-resolution imaging and spectroscopy to investigate the abundance, morphology and valence state of particulate iron in glacial sediments. Our results document the widespread occurrence of amorphous and Fe(II)-rich and Fe(II)-bearing nanoparticles in Arctic glacial meltwaters and iceberg debris, compared to Fe(III)-rich dominated particulates in an aeolian dust sample. Fe(II) is thought to be highly biolabile in marine environments. Our work shows that glacially derived Fe is more labile than previously assumed, and consequently that glaciers and ice sheets are therefore able to export potentially bioavailable Fe(II)-containing nanoparticulate material to downstream ecosystems, including those in a marine setting. Our findings provide further evidence that Greenland Ice Sheet meltwaters may provide biolabile particulate Fe that may fuel the large summer phytoplankton bloom in the Labrador Sea, and that Fe(II)-rich particulates from a region of very high productivity downstream of a polar ice sheet may be glacial in origin.

1. Introduction

Iron (Fe) is an essential micronutrient for marine phytoplankton, and its availability limits growth of primary producers in large parts of the world's oceans (Moore et al., 2013). Fe availability is therefore critical in dictating the strength of the ocean biological pump, which in turn affects atmospheric CO_2 concentrations and global climate (Moore et al., 2013). A critical control on the availability of iron in seawater is its solubility. In oxygenated waters, the more reactive and soluble ferrous oxidation state, Fe(II), readily oxidises to the ferric state, Fe(III), which is poorly soluble. Dissolved Fe^{2+} is more labile than Fe^{3+} in oxic environments, where it is thermodynamically unstable unless stabilised by organic colloids (Breitbarth et al., 2009; Lam et al., 2012). The majority of available iron in the oceanic euphotic zone is consequently thought to exist as nanoparticulate/colloidal Fe(III), varying in size, speciation and structure, and therefore in solubility and bioavailability (Raiswell and Canfield, 2012; von der Heyden et al., 2014). However, recent studies suggest that a particulate Fe(II) pool may play a significant role (Lam et al., 2012; von der Heyden et al., 2012). The speciation and minerology of Fe particulates appears particularly important in dictating bioavailability (Lam et al., 2012; Shaked and Lis, 2012; von der Heyden et al., 2012; Shoenfelt et al., 2017). Currently our understanding of the valence state of potentially bioavailable Fe sources in the ocean is limited due to measurement challenges (von der Heyden et al., 2012).

Glaciers and ice sheets are large sources of iron to the polar oceans, principally via iceberg rafted debris (Death et al., 2014; Duprat et al., 2016; Raiswell et al., 2016) and meltwater runoff (Schroth et al., 2011; Gerringa et al., 2012; Bhatia et al., 2013; Hawkings et al., 2014; Lyons et al., 2015; Hodson et al., 2017). Most potentially bioavailable Fe is delivered as poorly ordered oxyhydroxide nanoparticles, primarily ferrihydrite, which were identified by high resolution transmission electron microscopy (HR-TEM) and sediment extractions (Raiswell, 2011; Hawkings et al., 2014; Raiswell et al., 2016). Particulate Fe, especially ferrihydrite, has

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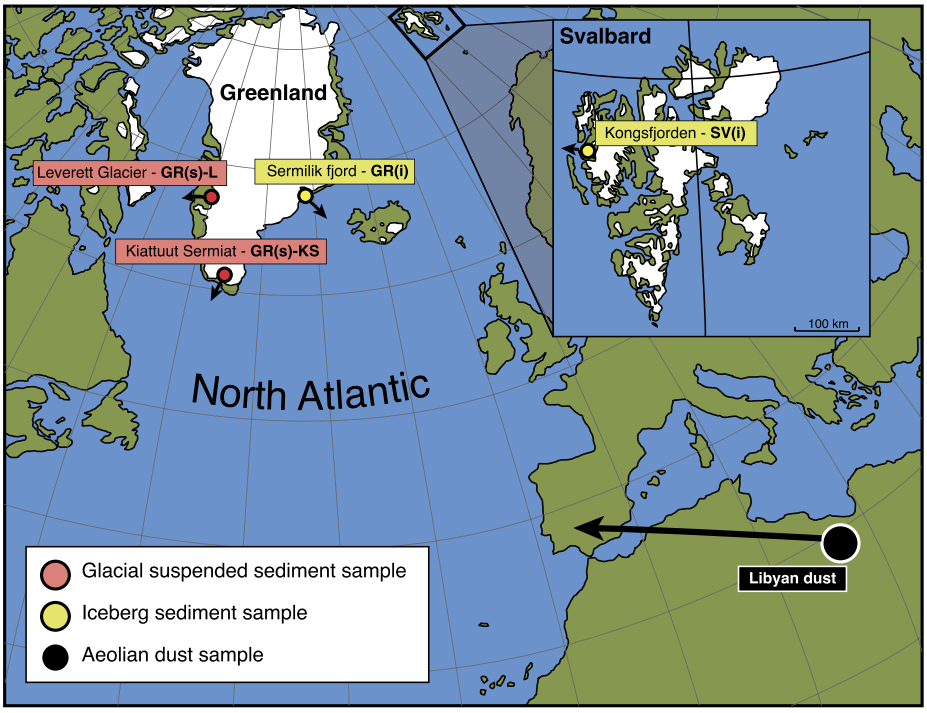

Fig. 1. Map of sample locations and source type. Two suspended sediment samples (red dots) and one iceberg sample (yellow dot) were collected from the Greenland Ice Sheet. One additional iceberg sample was collected from Kongsfjorden in Svalbard (insert, yellow dot). An aeolian dust precursor sample was also collected from Libya (black dot). This sample was also treated to simulate cloud-processing effects (Shi et al., 2012). Arrows indicate approximate path of transport to the ocean. GR = Greenland, SV = Svalbard. (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

already been demonstrated to be, at least to some degree, bioavailable to phytoplankton cultures (Smith et al., 2007; Raiswell and Canfield, 2012; Sugie et al., 2013; Shoenfelt et al., 2017). Glacial sediments may contain a range of particulate iron species, including a particulate and extractable Fe(II) component (Hopwood et al., 2014; Shoenfelt et al., 2017). Particulate Fe in marine waters around the Antarctic coastline has a distinctive Fe(II) dominated mineralogy associated with a region of very high primary productivity in the Southern Ocean (von der Heyden et al., 2012). In addition, Antarctic ice streams have been postulated to channel subglacial meltwaters from the continental interior to the coastal ocean (Le Brocq et al., 2013; Garabato et al., 2017), the fluxes of which may be elevated during glacial periods (Frisia et al., 2017). These meltwaters may be anoxic in places and contain high concentrations of Fe(II) (Wadham et al., 2013) that may be exported downstream in dissolved or (nano)particulate form to near coastal ecosystems (Annett et al., 2017). Thus, highly reactive Fe(II) bearing particles may originate from glacial input and may be stabilised via binding to inorganic or organic ligands (von der Heyden et al., 2012), which makes them an important source of potentially bioavailable Fe to marine biota.

Evidence for the export of biolabile Fe(II) particles from ice sheets is lacking, but here we have quantified the nanoscale mineralogical and spectroscopic characteristics of Arctic glacial meltwater suspended sediments and iceberg rafted debris. We determined the distribution and speciation of particulate Fe at high-resolution (30–50 nm/pixel) using synchrotron scanning X-ray microscopy (SXM), complemented by high resolution transmission electron microscopy (HR-TEM), energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) analyses. These analytical tools allowed us to assess the variations in the oxidation state and coordination environments of complex particles to determine the form of nanoparticulate Fe present, which influences its solubility and bioavailability. We show that glacially derived iron nanoparticles have a distinct speciation that suggests high bioavailability.

2. Methods

2.1. Sample source regions

Samples were collected from four glacial locations in the northern polar region, and one dust source to the North Atlantic (Fig. 1). The two suspended sediment samples were collected near the terminus of Leverett Glacier in southwest Greenland (GR(s)-L; 67.06°N, 50.17°W) and Kiattuut Sermiat in Southern Greenland (GR(s)-KS; 61.21°N, 45.33°W) (Hawkings et al., 2016), during May 2012 and June 2013 respectively. Both glaciers drain the Greenland Ice Sheet, but Leverett Glacier has a significantly larger hydrologically active catchment area (~600 km^2 vs ~36 km^2; Hawkings et al., 2016). One iceberg sediment sample was collected in Sermilik fjord, East Greenland (GR(i); 65.7°N, 37.9°W) in July 2014, and the other from Kongsfjorden in Svalbard (SV(i); 78.9°N, 12.1°E) in July 2013. These were compared to a precursor aeolian dust sample collected from Libya, and the precursor aeolian dust after simulated low-pH atmospheric processing (Shi et al., 2015). The Libyan dust precursor sample was collected from the Tibesti Mountains in South Libya, Western Sahara (23.6°N, 16.5°E; detailed description available in Shi et al., 2011).

2.2. Sample collection

Glacial meltwater and iceberg samples were collected by filtration onto a 0.4 µm polycarbonate (Whatman Cyclopore®) or 0.45 µm cellulose nitrate filter (Whatman®) as detailed elsewhere (Hawkings et al., 2014; Raiswell et al., 2016). Meltwater samples were collected in lab detergent and acid-washed 1,000 mL bottles (1% DECON for 24 h, 3× rinsed 18.2 $M\Omega\,cm^{-1}$ de-ionised water, 10% HCl for 24 h, then 6× rinsed with 18.2 $M\Omega\,cm^{-1}$ de-ionised water and dried in a laminar flow hood; Nalgene™ low density polyethylene). Meltwater samples were taken from a flowing section of the main river channel and filtered within 15–30 min of collection inside a designated clean lab tent or field hut (Hawkings et al., 2014, 2016). Iceberg samples were collected from a boat,